Spatial Distribution of Airborne PCBs in Milwaukee

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Author's Note and Acknowledgements

This report may contain explanations of concepts, such as those involved in interpreting statistics and the processes governing environmental cycling of PCBs, that the more technical reader may not require. At the same time, many find tables filled with numbers and statistics difficult to understand.

Attempts to balance the opposing needs of technically oriented readers and the general public has driven the overall formatting of this document. Tables of results and statistical comparisons are preceded and/or followed by text which highlights significant points about the information contained in the tables.

It should be noted that the author bears sole responsibility for the contents of the report, and for the conclusions drawn from the data.

Any study of this nature is the product of more than a single individual's work. Additional DNR personnel vital to this study include Mark Allen, lead worker for the Wisconsin Urban Air Toxics Monitoring program, and the site operators in Green Bay and Milwaukee, who collected the samples which have made this analysis possible.

A special thanks is extended to Al Spallato of the State Laboratory of Hygiene, who analyzed the vast majority of the samples reported here. His work has been of consistent quality, and his input over the years invaluable.

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Executive Summary

Introduction

The Wisconsin Urban Air Toxics Monitoring Program (UATM) routinely collects samples for the determination of PCB concentrations in air. These samples have been collected at a variety of locations around the state, beginning in 1991. Collection of PCB samples in Milwaukee began in late 1999, at the Sixteenth Street Health Center.

Over time it became apparent that results observed at the Milwaukee location were different from those obtained elsewhere in the state. Typically, a strong seasonal trend in concentrations is observed, with summer values being greater than those obtained in other seasons, and winter values being uniformly low.

At Sixteenth Street, however, this seasonal pattern was not as readily apparent. In addition, concentrations observed in winter at this site were frequently higher than annual maximum values seen in Green Bay, which had previously been the site with highest observed concentrations.

Enough data had been collected from the Sixteenth Street site by 2002 to confirm that the some factor or combination of factors in Milwaukee was indeed causing results to vary from the patterns observed in other areas, and an investigation into potential reasons was initiated. This search yielded information indicating that a current point source of PCBs to the atmosphere is operating relatively close to the Sixteenth Street site.

This information in turn led to an interest in conducting a multi-site PCB study in Milwaukee, to determine whether the concentrations observed at the Sixteenth Street site reflect typical ambient conditions in the urban area, or whether there are discernable differences between different locations in Milwaukee.

Funding was obtained for this study in late 2002, and two additional sites were established. One of the sites was located near a known PCB contaminated sediment hot spot in the Milwaukee River, while the second was located approximately equidistant between the two sites.

Sampling at all three locations was conducted from December, 2002 through December, 2003. Results of these samples, plus all earlier samples from the Sixteenth Street site are compiled in this report. Results from samples collected at the current PCB monitoring site in Green Bay (established in May, 1997), and from a site in Madison (established in June, 2002) are included for additional comparisons.

Summary and Conclusions

A total of 71 samples for PCB analysis were collected in Milwaukee during the course of this study. In addition, 70 additional Milwaukee samples were collected prior to the establishment of all three sites. Comparison between these samples, the 165 samples from Green Bay and the 34 samples from Madison reveal significant differences between the sites.

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In general, concentrations at the various sites conform to the following trend:
Sixteenth Street > SER Headquarters > Parkway School ≈ Green Bay > Madison. This observation holds true through the majority of the analyses applied to the data.

Significant seasonal trends are present to varying degrees in the data from all sites. In general, seasonal concentrations vary according to the following trend:
Summer > Spring ≈ Fall > Winter. These trends tend to be strongest at the sites furthest from known sources.

Sufficient data for annual trend analysis is present with the Sixteenth Street and Green Bay data sets. While the results from the former site do vary from year to year, no clear trend is apparent. In contrast, a significant abrupt decline in ambient concentration is apparent in the Green Bay data set, with results obtained between 1997 and 2000 being significantly higher than those obtained between 2001 and 2003. This observed difference in concentrations may reflect remediation efforts on the Fox River, which included the removal of a significant amount of contaminated sediment from the River in Green Bay during 1999 and 2000.

It should be noted that the EPA Cumulative Exposure Project cites a benchmark concentration of 0.45 ng/m^3 for PCBs. The benchmark concentration is intended to reflect an ambient level above which there may be concern for human health. Annual time weighted average concentrations observed at the Sixteenth Street site exceed this level in both 2000 and 2003. The overall time weighted average concentration derived from all data collected at this site is 0.44 ng/ m^3.

Comparison of the identity of aroclor patterns observed in the samples indicates that the Parkway School and Sixteenth Street sites are probably impacted by different sources. The patterns observed at the SER Headquarters site appear to reflect the influence of both suspected sources. These sources have been identified as the Milwaukee River and Estabrook Impoundment near Parkway School, and Miller Compressing near the Sixteenth Street site. It should be noted that additional unknown sources may be present, representing both environmental cycling of previously deposited material and potential ambient point sources.

Recommendations

Sampling should continue at the Sixteenth Street site for the foreseeable future. It should be recognized that the PCB concentrations observed at this location are impacted by a local source, and are thus not reflective of an overall urban average for Milwaukee. In addition, the duplicate sampler currently located in Green Bay should be moved to this site to provide direct evidence that our sampling in that area is within quality control guidelines.

If possible, funding should be obtained to increase sample frequency at Sixteenth Street to a one in six day schedule, from the current one in twelve day schedule. Funding to continue sampling at additional sites in the Milwaukee area would be desirable as well, to further characterize the urban area.

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Rationale

Ambient monitoring for polychlorinated biphenyl (PCBs) has been a part of Wisconsin's Urban Air Toxics Monitoring (UATM) program since it's inception in 1991. To date, samples have been collected in Green Bay (1991 through present), Wisconsin Rapids (1997 – 2000), Milwaukee (1999 through present), Trout Lake (2000 – 2001) and Madison (2002 – 2003).

In general, our results show a clear seasonal pattern, which is associated with environmental cycling of previously deposited material. In environmental cycling, meteorological conditions (primarily temperature) drive the volatilization of PCBs from contaminated soils, sediments and water. This pattern is characterized by strong statistical differences between seasons, with consistently low results observed in winter.

After sampling in Milwaukee for 2 years, however, it became clear that the typical seasonal pattern did not apply at the location we were collecting samples. At this site, we would frequently observe mid-winter values an order of magnitude greater than those observed at other UATM sites. Some mid-winter values have exceeded yearly maximum values in Green Bay.

Investigation of the DNR Air Emissions Inventory revealed a source that reports PCB emissions located approximately a kilometer north of the Milwaukee sampling site which could explain the observed discrepancy. In addition, there are some documented sediment hotspots in the Milwaukee area which could be contributing to ambient PCB concentrations as well.

This led to an interest in a spatial sampling study involving multiple sites in Milwaukee. Two additional sites were established at different locations in Milwaukee at the end of 2002, and sampling at all three sites conducted between 12/10/2002 and 12/31/2003.

This report evaluates all PCB results obtained in Milwaukee, from the start of sampling at the 16th Street Health Center site in October 1999 through the completion of the spatial distribution study at the end of 2003. In addition, results from Green Bay (May, 1997 through 2003) and Madison (June 2002 through 2003) are included for comparison.

Sampling Locations

A list of site designations and location names included in this study is presented in Table O-1 at the end of this section, along with sampling dates and local potential sources. The site designations are used to label data from the sites in tables and figures throughout this report.

Sampling in Milwaukee began on the roof of the 16th Street Health Center located about a kilometer south of the Menominee Valley in south Milwaukee. This is the primary

Urban Air Toxics Monitoring station in Milwaukee. The immediate neighborhood is mixed residential and commercial, although it is relatively close to the industrial concentration in the valley.

Additional Milwaukee sites added for the spatial study are at the DNR's South East Regional Headquarters located at North and Martin Luther King Boulevard, and at the Parkway School along the Milwaukee River Parkway in Glendale. The local neighborhood in both cases is generally residential and commercial.

The Parkway School site was chosen for its location near the Milwaukee River, about a kilometer north of the Estabrook Impoundment in Lincoln Park. This choice was made to provide a location near a known likely environmental cycling source of PCBs in Milwaukee.

SER Headquarters is not located near any known sources, but is located about halfway between the other two sites, and should therefore be influenced by both to some extent.

PCB Sampling in Green Bay has been conducted at three different locations. Only results from the most recent site are included in this report. This site is located on a rooftop in an industrial area approximately a kilometer from the mouth of the Fox River, and has been active since May 1997. Results obtained from a wide variety of sites during the Fox River Remediation Air Monitoring Study indicate that this site provides a good urban background concentration for Green Bay.

Sampling in Madison was conducted at the East High School site, located on the East High School athletic fields. This site is located between a residential and an industrial area. The nearest known potential source of PCBs to the atmosphere is located about 5 miles away at the Nine Springs Wastewater Treatment Works, where a settling basin is known to hold PCB containing sediments.

Table O-1: Sampler Locations

Site Designation	Location Name	Dates Sampling	Type	Potential PCB Sources Within @ 1 Kilometer
GB	Prange Way, Green Bay	6/97 - present	rooftop	Green Bay, Fox River
SS	16th St, Milwaukee	10/99 - present	rooftop	Miller Compressing
ME	Madison East High	6/02 – 12/03	rooftop	None known
HQ	SER HQ, Milwaukee	11/02 – 12/03	platform	None Known
PS	Parkway School, Glendale	12/02 – 12/03	rooftop	Estabrook Impoundment

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Source Descriptions

Each of the primary potential sources has different characteristics. One purpose of this study is to compare local impacts associated with environmental cycling sources, with those near a self-identified ambient point source of PCBs. This section explores potential differences between the known sources that may provide a means to distinguish their effects on the different sites. Table O-3 at the end of this section summarizes the sources and their differences.

The lower Fox River from Little Lake Buttes Des Morts in Neenah and Menasha, to the mouth at Green Bay contains what are probably the most contaminated sediments in Wisconsin. A long-term remediation program is in process, where the sediments will be removed and buried in landfills to remove the PCBs from the river.

Several feasibility and design demonstration projects have been conducted at different hot spots along the river, most notably the Sediment Management Unit 56/57 Demonstration Remediation Project in Green Bay, during which more than 1300 pounds of PCB were removed from a major deposit during 1999 and 2000. An extensive air sampling program to evaluate impacts associated with the sediment removal was conducted in 1999.

The original source for these deposits was a number of paper mills along the river that made and recycled carbon-less copy paper, which was originally made by a process that impregnated paper with small ink-filled PCB-containing beads. Aroclor 1242 was the most common mixture used in these beads. Pressure on the beads would cause them to burst, releasing ink which then marked the copy.

Industrial practices during manufacturing and recycling of this type of paper led to deposits of the material on the riverbed over an extensive portion of the river. Water action on these deposits has transported a significant quantity of PCBs into Green Bay as well.

The Fox River and Green Bay have been the subject of a significant body of research which helped define the environmental cycling model, wherein an equilibrium between sediments and water, and water and air drives the volatilization of PCBs.

Several different potential environmental cycling sources could have an influence on the sites in Milwaukee. The Milwaukee, Menomonee and Kinnickinnick Rivers have all been shown to contain PCB contaminated sediments to varying degrees, as well as the harbor and Lake Michigan itself. The Milwaukee River and upstream tributaries have several significant PCB deposits that have been characterized by extensive sediment sampling.

One of the identified hotspots for PCB containing sediments is the Estabrook impoundment, located in Lincoln Park. Between the dam, which forms the impoundment and Thiensville to the north, the riverbed is estimated to hold over 5200 kilograms of

PCBs. The majority of this is in the Lincoln Park lagoon, a short way upstream from the Estabrook dam.

The most contaminated portion of these sediments is located on the side of the impoundment that receives Lincoln Creek, which is the suspected route of entry for the PCBs. Limited sediment sampling along this creek shows the presence of PCBs, but the original source for the contamination is not known.

Water level management protocols for this site include a winter draw down that exposes much of the contaminated sediment from late fall through early spring each year. Whether or not this has an effect on local air concentrations is investigated with the Parkway School site data.

In addition to the sediments in the lagoon, a low water dam is in the river a short way upstream of the Parkway School. The water flowing over the dam is aerated by turbulence. This action may increase volatilization of PCBs introduced to the river from upstream contaminated sediments.

A congener analysis study conducted by the U.S. Geological Survey between 1993 and 1995 revealed that upstream sources to the Milwaukee River tend to be composed of Aroclors 1254 and 1260, while the Lincoln Park sediments tend to contain Aroclor 1242. Differences in the Aroclor patterns observed at the different sites may help to determine the sources of the observed PCBs.

The Estabrook dam and Lincoln Creek are also USGS water monitoring sites, from which water flow, ice cover and some temperature data was available. This data is included in the correlation and regression statistics in the Source Analysis section. The other potential environmental cycling sources in Milwaukee are not as well characterized, and no data has been incorporated to represent these sources.

Several industrial sources in Wisconsin claim current PCB emissions. These include Miller Compressing, a metal recycling facility located at Sixteenth and Bruce Streets in Milwaukee; Kadant Grantek, a secondary recycle paper sludge drying facility in Green Bay; and the Green Bay Metropolitan Sewerage District. Most of the following discussion is in reference to Miller Compressing.

The source material for the PCB emissions from Miller Compressing is called “white goods”, and is composed of old appliances which are shredded for their scrap value. Appliances made before the early 1980’s are likely to contain PCBs in miscellaneous electrical components, such as capacitors. The most frequent commercial aroclor mixture used in this application was Aroclor 1242, although others were also commonly used.

When the appliances are shredded, any PCBs present are released to the environment. Some of this material will be volatilized and may escape. The above ambient temperatures generated during the process will help drive this process. Some of the PCBs that are released are captured by pollution control equipment, and a portion does not volatilize and may be present in the shredder fluff or deposited in the shredder.

Emission rates reported by the facility are annual estimates of total PCB based on the throughput of white goods over the course of a year. The identity of the likely aroclor mixtures emitted is not reported. This data has been reported for the years 2000 through 2002.

The data for 2003 is not yet published, and so can not be used to evaluate results of the spatial sampling in Milwaukee. Emission rates from earlier years are qualitatively compared with Sixteenth Street data to determine whether this factor can help explain annual differences in the results from this site.

The Green Bay facilities that report PCB emissions are primarily a resuslt of processing materials (paper sludge and municipal wastewater) which in Green Bay contain small quantities of PCB as a result of the general contamination in the area. Information on the aroclor composition of these emissions is not available, but it is likely that Aroclor 1242 forms a major component.

Table O-2 below presents annual PCB emission estimate submitted to the Air Emission Inventory for these facilities from 1997 through 2002. Note that non-reporting of an emission rate does not necessarily mean that PCBs were not emitted. The overall accuracy of this data is unknown.

Table O-2: Reported PCB Emissions, lbs/year

Facility	1997	1998	1999	2000	2001	2002
Miller Compressing	NR	NR	NR	0.78	1.81	1.18
Kadant GranTek	1.75	1.43	NR	NR	NR	1.53
GBMSD	NR	NR	NR	0.67	0.57	0.56

Table O-3 below summarizes the information for each potential source in Milwaukee and Green Bay.

Table O-3: Characteristics of Potential PCB Sources in Milwaukee and Green Bay

Source Name	Type	Aroclor
Fox River & Green Bay	Cycling	1242
Milwaukee River	Cycling	1254 & 1260
Estabrook Impoundment & Lincoln Creek	Cycling	1242
Miller Compressing	Point	1242, others?
Kadant GranTek	Point	1242, others?
GBMSD	Point	1242, others?

It should be noted that this is not an exhaustive list of PCB sources that may influence the results of this study. In addition to other potential industrial sources which either are not aware of or simply do not report their PCB emissions, a potential multitude of small environmental cycling sources are present where-ever an electrical transformer has burst or caught fire in the past. No attempt has been made to identify further specific sources.

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Sampling and Analytical Protocols

Samples were collected by DNR personnel following EPA Method TO-4, Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD), as outlined in the DNR Air Monitoring Handbook, Method OP 8.5, Sampling Semi-Volatile Organic Compounds Using a PS-1 Sampler.

Analysis was performed by the State Laboratory of Hygiene (SLOH), Air Chemistry Section, following the protocols in their internal Standard Operating Procedure (SOP) titled "Ambient Air for Pesticide and PCB Residues – Modified EPA Method", SOP# 1920, revision 2.1, dated September 1, 1999.

Experience in monitoring air has shown wide seasonal variability in ambient PCB concentration. The Wisconsin Urban Air Toxics monitoring program PCB sampling protocol calls for a 72 hour sample period between April and November, and a 144 hour composite of 2 sample periods for the remainder of the year.

Based on a 1000 m^3 sample, and a 0.1 ug total PCB as Aroclor laboratory reporting limit, method detection limits are estimated to be about 0.1 ng/m^3 during the 72 hour sampling portion of the project. Detection limits during the 144-hour portion of the test are on the order of 0.05 ng/m^3. Following this protocol, we are able to detect PCBs in nearly every sample collected.

Results are quantified by comparing the fingerprint observed with those of known Aroclor mixtures. This method is not as detailed as quantifying individual congeners, but it has proven to be sufficient for the purposes of our monitoring program. While environmental degradation and other effects influence the composition of ambient samples, experience has shown that the majority of the samples collected as part of the UATM program generally conform to a pattern similar to Aroclor 1242.

Samples collected during this study were about equally split between those which were clearly dominated by Aroclor 1242, and those which contained a more complex mixture corresponding to a combination of Aroclors 1242, 1248 and 1254. The distribution and pattern of the different Aroclor mixtures is discussed after the quantitative analysis.

Sample Handling

Each sample was accompanied by a corresponding field sheet including the following information: unique field number, identification of site by name and site number, unique sample head and sampler identifiers, sampler calibration code, and pre- and post- sample flow and elapsed timer readings. A comment section included space for observations, including reasons for void samples.

All samples were collected using standard Anderson or General Metals Works PUF sampling heads. Each head was uniquely identified for sample tracking. Each site was assigned a set of sample heads that were used exclusively at individual sites, thereby decreasing the chance of cross contamination.

Data Quality Objectives

Study related data quality objectives in this report include project completeness, and blank sample material background levels. The completeness criterion is evaluated at both the field and analytical levels. Duplicate sampling was not part of the Milwaukee sampling, as no additional samplers were available for their collection. The PCB sampling site in Green Bay includes duplicate sampling, the results of which are included.

The quality objective for duplicate samples according to EPA Method TO-4 is ±25% relative percent difference. Most DNR collected duplicates have historically been within ±15% relative percent difference (RPD).

Accuracy in sampling and analysis is evaluated using spiked duplicate and spiked blank samples. These samples are not collected every year. This report includes spiked samples from the entire history of the WUATM program to provide an overall picture of the effectiveness of our sampling protocols.

Evaluation of analytical recovery is based on the spiked blank, while collection efficiency is evaluated by comparing the spiked duplicate with the associated ambient sample. Recovery and collection efficiencies of 100 ±25% are considered acceptable performance.

The data quality objective for blank samples is an undetectable quantity. Two main types of blanks are incorporated into this study. A lot blank consists of a PUF plug submitted for analysis directly from the manufacturer, without being opened before receipt by the laboratory. Each PUF plug manufacturing lot received has a blank submitted before sampling commences.

A field blank is a sample that has been prepared for sampling through all stages, but without drawing air through it. Sampler failures provide blanks measuring potential contamination associated with passive ambient exposure.

Calculation Protocols

The use of seasonally variable sampling times requires time weighted averaging of results to provide accurate seasonal and annual average values. Each 144-hour sample is collected during a time frame equivalent to two 72-hour samples, and so the resulting value is included twice in the statistical permutations for these calculations. Likewise, the handful of samples collected on a 1in 6 day frequency in Green Bay during the Fox River Remediation Demonstration Air Monitoring Project are averaged across the 1 in 12 day sampling periods corresponding to the remainder of the project.

Data evaluated in this manner includes the complete set from each site. Statistical analysis to compare annual and seasonal trends both within and between sites employ Microsoft Excel data analysis tools, including summary statistics and two sample t-tests assuming unequal variances. It should be noted that results in all tables are rounded, while values used in the calculations are not. This may lead to some apparent discrepancies in calculated results.

The inter-site comparisons by sample and correlation with additional data such as meteorological and USGS data are made on a per-sample basis, rather than the time weighted averaging used for the seasonal and annual trends. Data incorporated into the inter-site comparisons includes all results obtained since the beginning of sampling at the 16th Street (October 15, 1999), while the correlation are made with as complete data sets from each site as possible.

Statistical analysis to evaluate correlation with non-PCB data employs the linear regression r-squared and the correlation data analysis tools. The r-squared function is a measure of the linearity of the relationship between two parameters, with a value of one indicating identical data sets and a value of zero indicating no relationship between the sets. An r-squared value of 0.6 or greater (a 60% linear relationship between the two parameters) is considered significant.

The correlation function is a measure of how different parameters vary with respect to each other. A positive correlation indicates that larger values of one parameter (such as ambient PCB concentration) tend to be associated with larger values of the second parameter, while a negative correlation indicates that small values of one set tend to be associated with large values of the second set. Values can range from –1.0 to +1.0, with the statistical significance of any particular value related to the size of the sample sets being compared.

It is important to note that a high correlation coefficient does not necessarily indicate cause. The correlation coefficient merely measures how closely each data set happens to vary with respect to the other. For example, water temperature in Lincoln Creek and air temperature in Milwaukee are highly correlated with each other. The high correlation in this case highlights a relationship between two parameters that are influenced by a separate cause, the seasonal changes in solar radiation.

Treatment of LOD and LOQ Samples

A common misperception about analytical results such as those presented here is that a number reported is a measurement equivalent to counting apples in a basket. Trace analysis doesn't really work this way. Results reported present the most probable value obtained at a particular time and place, given the constraints of the methods used. Each phase of the sampling and analysis includes potential sources of error.

However, many samples can be adequately presented as though the chemical of interest was being counted. This is because analysis limits of error are known and within acceptable parameters as defined by standard methods. This approach facilitates the presentation of study results.

There are two important statistically determined values called the Limit of Detection (LOD) and the Limit of Quantitation (LOQ). The LOD is the lowest amount of the compound of interest that can be clearly distinguished from the analytical background. A non-detect means the observed concentration was less than the statistically determined LOD, not that there was none of the compound of interest present.

The LOQ is the lowest amount of analyte that can be definitely quantified, and is conventionally set at three times the LOD. Results between the LOD and LOQ are technically considered estimates, with less assurance that the values are "correct" as reported than for results above the LOQ. In a sense, any result obtained in this range could actually be any concentration within the range, with approximately equal probability.

Ideally, all results obtained from a test of this nature would be above the LOQ, thereby removing any difficulty arising from evaluating values with less confidence. However, samples with either non-detectable or barely detectable results are obtained, and evaluation of these results is necessary.

The problem of incorporating non-detects into a numerical data set can be addressed in several ways. One approach is to disregard non-detected values entirely. This has the advantage of averaging only clearly determined values. The problem with this method is that the information provided by the presence of non-detect samples is lost, and the resulting averages will be artificially high.

Pretending that the non-detects represent samples where there was none of the analyte present, and setting the value of such samples at zero is another option, but this approach also provides a poor reflection of reality. Non-detects do not necessarily represent a zero value. In fact few, if any, of the non-detects obtained truly represent the absence of PCBs in the atmosphere.

The most that can be said about non-detects is that ambient concentrations are less than the detection limit. With this in mind, the method chosen to incorporate these values into the data set is to substitute the detection limit for non-detect results. This approach incorporates all data in a manner that provides the maximum possible true value for the sampling period, thereby providing the worst case realistic analysis of impacts. The rate of detection (number of detects / number of samples) provides an indication of overall reliability of the reported values. The only non-detects reported during this study were obtained at the Madison East High site.

Similarly, there are different approaches to rationally incorporating results obtained between the LOD and LOQ. For simplicity sake, these values are treated in the same way as values above the LOQ, in other words, as if they represent the most probable concentration during the sampling period. The variable rate of samples exceeding the LOQ at the different sites provides an additional tool for comparing results.

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Data Quality Review

Completeness

The completeness parameter evaluates the ratio of valid samples collected to scheduled sampling days. As a general rule of thumb, a completeness of 75% is considered acceptable for applying the data to a description of the overall ambient conditions during the sampling period. All sites exceeded 90.0% completeness.

The table below shows sampling completeness from all sites. The table separates the "total" sampling period from the "intensive" sampling period, which includes only the 25 sampling periods that all three sites in Milwaukee were operational. The PS and HQ sites are not evaluated under the "total" sampling period, as they were only in existence during the intensive sampling. Completeness at Madison East is based on 37 potential sampling periods at this site.

It should be noted that there were two samples at SER Headquarters and one at 16th Street that were collected for 72 hours instead of the scheduled 144. Several other samples at SER HQ did not run the entire sampling period. These samples are counted as samples and included in the completeness, as are makeup samples that were obtained on alternate sampling days. The most frequent causes of missing or short samples are power problems with the sampler, and motor burnouts.

Table Q1: Sampling Completeness (number of samples collected vs. scheduled runs)

Site	Green Bay			Sixteenth St			SER HQ		Parkway School		Madison East	
	Possible	Act	% Com	Act		% Com	Act	% Com	Act	% Com	Act	% Com
Total	169	165	97.6%	100	92	92.0%	25	***	24	***	34	91.9%
Intensive	25	25	100.0%		24	96.0%	23	92.0%	24	96.0%	23	92.0%

Blank Samples

A total of 24 blanks were collected between 1997 and 2003, representing 7.1% of the ambient samples submitted from these sites. Both field blanks (17) and lot blanks (7) were collected. Field blanks are samples that were treated as an ambient sample without drawing a significant quantity of air through the cartridge.

One of the field blanks from the HQ site was obtained from a sampler which failed to run properly. Blanks obtained in this manner are the most representative of general sampling conditions, and provide a good indication of whether extraneous contamination in the field is a problem.

There were no detectable quantities of Aroclor in any of the blank samples submitted. The implication of this is that neither the sample material nor the handling procedures introduced contamination that would interfere with analysis. As such, no results are modified for background values in the discussion presented.

Table Q2: Blank Samples by Type and Site

Blanks	Total	SS	HQ	PS	GB	ME
Field	17	1	2	1	3	4
Lot	7					

Duplicate Samples

Duplicate sampling was conducted at the Green Bay site between 2000 and 2003. And at the Wisconsin Rapids site between 1997 and 2000. Only the Green Bay duplicates are included here.

A total of 13 pairs of valid duplicate ambient samples were submitted to the laboratory for analysis. This represents 3.8% of the total samples submitted. Of these 13 pairs, 12 (92.3%) are within the quality control guideline of ±25% Relative Percent Difference (RPD), with an overall average of ±12.4%. In addition, 11 of the sample pairs are within ±12.5% RPD. The single failed sample (collected in 2000) has an unclear chain of custody that raises questions as to its validity. Excluding this sample yields an average RPD of ± 7.3%.

The table below presents all non-spiked duplicate data. in nanograms total PCB as Aroclor per cubic meter. The sample that failed the criteria is in ***italics*** (17-Jun-00). No results are excluded from data analysis on the basis of the duplicate sample results.

Table Q-3: Duplicate Sample Results (ng/m^3)

Date	Primary	Duplicate	Average	RPD%	Date	Primary	Duplicate	Average	RPD%
17-Jun-00	***0.19***	***0.41***	***0.30***	***-74.5%***	**26-Apr-02**	0.15	0.13	0.14	12.2%
21-Oct-00	0.30	0.28	0.29	4.5%	**13-Jun-02**	0.20	0.21	0.21	-5.0%
02-Dec-00	0.11	0.12	0.12	-1.5%	**11-Oct-02**	0.17	0.18	0.18	-8.1%
14-Mar-01	0.09	0.09	0.09	6.9%	**27-Jan-03**	0.06	0.06	0.06	-7.3%
06-Jun-01	0.33	0.30	0.31	6.9%	**03-May-03**	0.15	0.16	0.15	-5.2%
10-Sep-01	0.20	0.23	0.21	-15.7%	**19-Aug-03**	0.25	0.27	0.26	-6.8%
04-Dec-01	0.10	0.09	0.10	7.3%					

Spiked Samples

Method accuracy is measured by adding a known quantity of Aroclor 1242 to several samples before deployment in the field. Each set of spiked samples includes an ambient sample, a spiked duplicate ambient sample, and a spiked blank. A regular field blank is typically submitted at the same time.

The blank serves as a blind check on the laboratory's ability to quantitatively recover a known amount of PCB. Evaluation is simply the direct ratio of the lab results to the quantity added. The quality control criterion for all spiked samples is a recovery of 100 ± 25%. The ambient/duplicate pair are evaluated both for recovery and duplicate precision.

There are two sources of Aroclor to the duplicate sample: the quantity initially added, and the ambient air during sampling. Evaluation of the spiked duplicate results involves several assumptions to account for this. First, the primary ambient sample results are assumed to accurately reflect ambient concentrations, and the duplicate sample volume is used to determine the theoretical ambient loading to the PUF cartridge. This loading is then subtracted from the actual results to obtain a recovery value. The table below presents results of this calculation.

A single recovery sample (from 2003) failed the QC criteria. The reason for the failure is most likely an operator error. A graduated pipette (±10% by volume accuracy) was used to add the spiking solution to the PUF instead of the proper volumetric pipette (±1% accuracy). In this case, the spiked blank passed its recovery criteria, while the duplicate failed.

Overall average PCB recovery measured in this way is 93.9% including all samples. If the failed sample and its accompanying spiked blank are disregarded on the basis of the preparation error, the overall average recovery becomes 95.8%. In either case, the overall recovery during the history of WUATM PCB sampling is within the QC criteria, hence all samples are included in the data analysis.

Table Q-4: Analytical Recovery (ug)

Date	Type	Aroclor Added	Recovered	% Recovery
12-Dec-95	Blank	4.00	4.0	100.0%
12-Dec-95	Duplicate	4.00	3.7	92.0%
28-Jul-98	Blank	0.27	0.2	85.2%
28-Jul-98	Duplicate	0.27	0.2	74.8%
19-Oct-99	Blank	0.98	1.0	101.9%
19-Oct-99	Duplicate	0.98	1.0	106.2%
24-Nov-99	Blank	5.44	5.2	95.6%
24-Nov-99	Duplicate	5.44	6.0	111.0%
24-Sep-03	Blank	0.75	0.79	105.3%
24-Sep-03	***Duplicate***	***0.75***	***0.5***	***67.3%***

Spatial Distribution of Airborne PCBs in Milwaukee, Wisconsin
Data Quality Review

Meteorological Data

Temperature, wind speed and wind direction are the meteorological parameters included in the data analysis. These data were obtained from several sources.

In Milwaukee, a number of air monitoring sites collect meteorological data, including SER Headquarters and the 16th Street Health Center site. Wind speed and direction data collection at the latter site began during 2003, and so is not present for the entire study period. Because not all of the sites involved in this study were able to provide their own meteorological data, the choice was made to obtain the data from all Milwaukee locations to provide overall city averages.

Individual site data were vector mean averaged over entire sample periods (72 to 144 hours) and compiled. The number of sites for which data were available for each sampling period ranged from one to five. Comparisons between the vector mean averaged data showed that most sites provided very similar results most of the time. Results from each different site were then averaged together to provide an overall average for each sampling period. These values were then used to investigate correlation between observed concentrations and meteorological parameters.

The Milwaukee data also provide the opportunity to do a wind sector analysis based on how many hours per sampling period the wind was coming from a particular sector. For this evaluation, a total of 8 wind sectors were defined, and the ratio of hours of wind from each sector versus the total hours of sampling used to investigate correlation. This analysis is slightly different than using the vector mean averaged wind speed and direction over the entire sampling period, because the averaging calculations can mask the presence of widely divergent wind directions which may have occurred at different times during the sample run.

Meteorological data for Green Bay was obtained from the National Weather Service site at Austin Straubel Airport in Green Bay. Daily average values were provided, which do not allow for the sector evaluation described above.

Madison meteorological data were derived from two sources. A wind speed and direction sensor was installed at the Madison East site near the end of 2002. Unfortunately, the installation was not completed, so that the sensor is mounted on a rooftop tripod rather than a 10-meter tower. The data are therefore considered somewhat suspect, and are not intended for submission to the central EPA Air Quality database.

Data from 2003 from this site were available, and have been used in the data analysis. Wind speed and direction data for sampling periods in 2002, as well as all temperature data, were obtained from the Weatherman.com website as there are no other DNR or National Weather Service meteorological sites in Madison. Sector analysis as described for the Milwaukee data was not attempted.

Spatial Distribution of Airborne PCBs in Milwaukee, Wisconsin
Discussion of Results

Results Overview

Overall results of analysis for all sites ordered from maximum to minimum averages are presented in the table below. Average, maximum and minimum values are reported are in ng/m^3 calculated on a time weighted average basis. Additional parameters include percent relative standard deviation (a measure of the variability of the data), the number of samples, the number of detects (>LOD) and detection rate, and the number of samples above the LOQ (>LOQ) and its associated rate. The final reporting parameters are the percentage of samples exceeding 0.3 and 0.45 ng/m^3 , respectively.

Results from the Parkway School (PS) site in Milwaukee include an extreme statistical outlier (in ***italics***). This value represents the highest concentration of PCBs observed during this study, and the second highest obtained from all regular UATM monitoring. No obvious sampling or analysis error is associated with this sample, so that it remains a valid environmental sample, although it apparently represents an unusual event. However, this single sample significantly alters the reported values. Data from this site are reported both with and without this outlying value throughout this report (see the Data Evaluation section).

Results from Madison East (ME) are reported both with the non-detects calculated at the detection limit, and with the detects ignored for comparison. Note that all further analysis including the Madison data incorporates the non-detects evaluated at the detection limit.

Table R-1: Ambient PCB Concentrations in Milwaukee, Green Bay and Madison

Site	Average	Max	Min	RSD	Samples	> LOD	Rate	> LOQ	Rate	> 0.3	> 0.45
SS	0.44	1.49	0.05	67.2%	93	93	100.0%	85	91.4%	68.8%	43.0%
HQ	0.28	0.60	0.07	54.9%	25	25	100.0%	18	72.0%	52.0%	24.0%
PS	0.25	***2.13***	0.06	145.2%	24	24	100.0%	9	37.5%	29.2%	12.5%
PS - out	0.19	0.56	0.06	65.4%	23	23	100.0%				
GB	0.22	0.76	0.05	57.1%	171	171	100.0%	67	39.2%	26.9%	4.7%
ME, + ND	0.12	0.34	0.04	62.4%	34	30	88.2%	1	2.9%	2.9%	0.0%
ME, - ND	0.13	0.34	0.05	57.2%	30						

Note that with the exception of the single outlying sample at Parkway School, all relative standard deviations are less than ±70%, indicating generally consistent data were obtained from each site. All sites have a greater than 75% rate of detection, but only the 16th Street site has more than 75% of the sample results obtained above the LOQ, while only a single sample from Madison was above this level. The implication of this is that the Madison data set, as well as those from Green Bay and the Parkway School site, may be somewhat less reliable than those from 16th Street and SER Headquarters.

Determination of the statistical significance of results from different sites was accomplished using a series of two-sample t-tests (Table R-2).

Spatial Distribution of Airborne PCBs in Milwaukee, Wisconsin
Discussion of Results

Reported parameters include the mean, variance and number of samples (n), and t-test P-values with associated degrees of freedom (df). The P-value is a measure of the probability that the results represent statistically distinguishable sample sets. P values of 0.05 or less indicate a 95% or greater probability that the sample sets are different. These values are tabulated in ***italicized boldface***. The Green Bay data have been separated into two separate periods for this comparison. The reasons behind this are discussed in the Annual Trends section below. Madison data is calculated with the non-detects evaluated at the detection limit.

Table R-2: Statistical Comparison of Results be Site

Site	Mean ng/m^3	Variance ng/m^3	n	SS P (df)	HQ P (df)	PS P (df)	PS – Out P (df)	GB 97-00 P (df)	GB 01-03 P (df)
SS	0.44	0.088	121						
HQ	0.28	0.024	32	***8.1E-05 (96)***					
PS	0.25	0.137	31	***0.013 (40)***	0.699 (40)				
PS - out	0.19	0.016	30	***1.6E-10 (113)***	***0.014 (59)***				
GB 97-00	0.27	0.017	106	***2.1E-08 (170)***	0.581 (45)	0.870 (32)	***0.007 (48)***		
GB 01-03	0.17	0.009	91	***4.6E-17 (150)***	***3.5E-04 (29)***	0.209 (31)	0.349 (40)		
ME	0.12	0.006	43	***4.0E-21 (153)***	***2.1E-06 (42)***	0.053 (32)	***0.007 (43)***	***2.2E-14 (131)***	***0.001 (102)***

Differences between the sites are highly statistically significant when the outlying value obtained at the Parkway School site is excluded (PS – out). Note also that Green Bay data between 1997 and 2000 are indistinguishable from the SER Headquarters site, while the data collected between 2001 and 2003 are indistinguishable from the Parkway School site, when the outlying value is excluded.

Before further investigation into the significance and potential causes of the observed differences between sites, each individual site is evaluated for annual and seasonal trends.

Discussion of Unusual Event at Parkway School

The single highest value observed among the samples reported here was collected at Parkway School between July 14 and July 17, 2003. There are no apparent sampling artifacts or accidental exposures of the sampling media that could be used to discount the value, so it remains a valid environmental sample.

The results of this sample are nearly four times higher than that of the next highest sample collected at this site, and nearly 1.5 times higher than the highest concentrations observed at Sixteenth Street. The aroclor pattern observed in the sample have been characterized as a mixture of Aroclors 1242, 1248 and 1254, which is somewhat typical for this site.

Winds during this sampling period were calm 20% of the time, from the west 24%, from the south 19%, from the southwest 12% and from the northwest 12%. Known and suspected sources in this area are primarily located to the south and southeast.

No real explanation behind the concentration observed during this event has been found. Although the value has been included in the data analysis, the extreme difference between it and the remaining values in the Parkway School data set render most comparisons statistically insignificant. When the value is excluded on the basis that it represents an unusual event and is a statistical outlier, many of the comparisons are seen to be significant.

Annual Trends

Data from the 16th Street Health Center and Green Bay sites is sufficient for an analysis of annual trends. In each case, samples collected during the first year of site operation (1999 and 1997, respectively) are excluded from the following analysis, on the basis that insufficient samples were collected to represent a valid annual average.

The table on the following page presents time weighted average annual mean concentrations obtained from each of these sites. Reporting format is the mean ± the standard deviation in ng/m^3, followed by the number of samples in parenthesis. Values were obtained using the descriptive statistic data analysis tool in Microsoft Excel. Figures R-1 and R-2 on the following page display this information graphically.

Table R-3: Annual Mean PCB Concentrations in Milwaukee and Green Bay

Site	*1998*	*1999*	*2000*	*2001*	*2002*	*2003*
SS			0.51 ± 0.34 (27)	0.35 ± 0.22 (30)	0.40 ± 0.24 (29)	0.56 ± 0.35 (29)
GB	0.26 ± 0.09 (23)	0.23 ± 0.13 (30)	0.25 ± 0.12 (28)	0.17 ± 0.09 (30)	0.17 ± 0.09 (29)	0.17 ± 0.11 (32)

Note that the annual mean concentrations observed at the 16th Street site vary from year to year without an apparent trend, while those from Green Bay appear to decrease after 2000. Investigation of whether or not there are statistically significant differences between the annual means of each individual site was made using a series of two-sample t-tests. Results from these tests are shown in the tables below.

Reported parameters include the mean, variance and number of samples (on the left hand half of the table), and the degrees of freedom (to the right and above the asterisks on the right side of the table) and t-test P-values (to the left and below the asterisks). P values of 0.05 or less are tabulated in ***italicized boldface***.

Table R-4: Statistical Comparison of Annual Concentrations at 16th Street

Year	Mean ng/m³	Variance ng/m³	n	2000 P \ df	2001 P \ df	2002 P \ df
2000	0.51	0.115	27			
2001	0.35	0.048	30	0.051 (44)		
2002	0.40	0.056	29	0.181 (46)	0.435 (56)	
2003	0.56	0.121	29	0.592 (54)	***0.010 (47)***	0.051 (49)

Table R-5: Statistical Comparison of Annual Concentrations in Green Bay

Year	Mean ng/m³	Variance ng/m³	n	1998 P \ df	1999 P \ df	2000 P \ df	2001 P \ df	2002 P \ df
1998	0.26	0.009	23					
1999	0.23	0.017	30	0.291 (51)				
2000	0.25	0.015	28	0.667 (49)	0.552 (56)			
2001	0.17	0.007	30	***0.000 (46)***	***0.032 (50)***	***0.004 (48)***		
2002	0.17	0.008	29	***0.001 (47)***	0.061 (51)	***0.010 (50)***	0.759 (57)	
2003	0.17	0.011	32	***0.001 (51)***	***0.049 (55)***	***0.008 (54)***	0.935 (59)	0.840 (59)

Note that with the samples from the 16th Street site, only the years 2001 and 2003 are statistically distinguishable at 95% confidence. This information, combined with the mean values, demonstrates that Milwaukee values vary without an observable trend developing. The Green Bay P-values, however, appear to indicate that years before 2001 are higher than those after 2000 are.

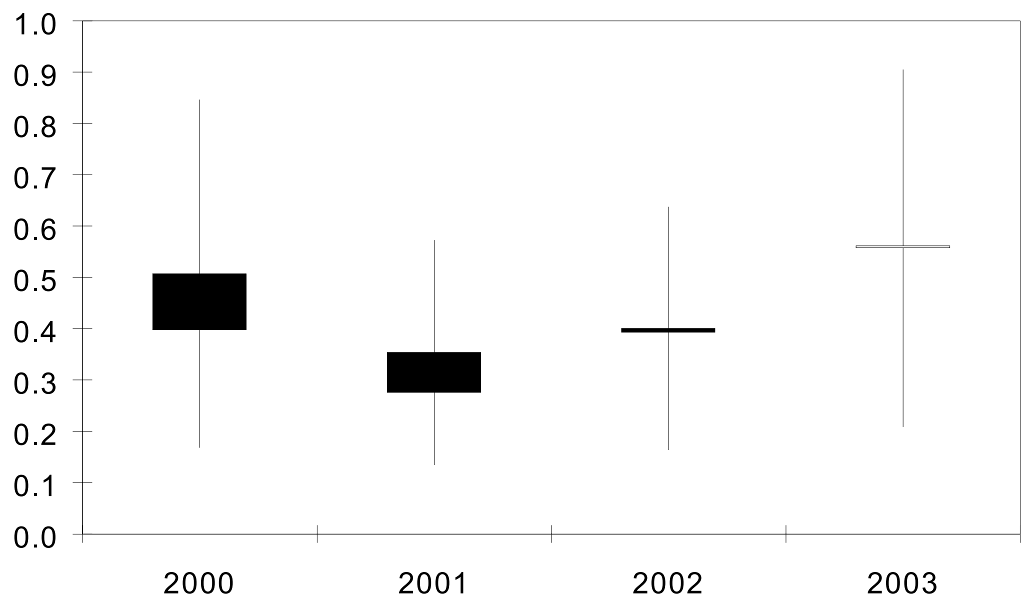
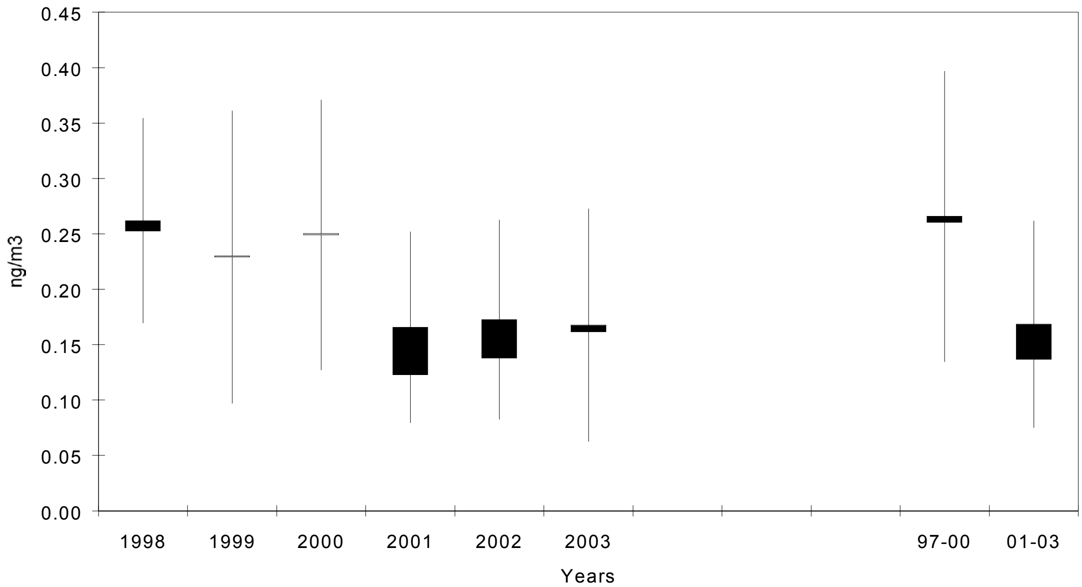


Figure R-1: Sixteenth Street Annual Trends

Figure R-2: Green Bay Annual Trends



Further investigation of the apparent trend in the Green Bay data is accomplished by comparing samples collected before and after 2000. Results of this two-sample t-test are shown in the table below.

Table R-6: Statistical Comparison of Sampling Periods in Green Bay

Period	Mean	Variance	Samples	df	P(T<=t) two-tail
97-00	0.27	0.017	106	189	***7.E-09***
01-03	0.17	0.009	91		

Note that with the size of the sample sets, a high confidence can be assigned to the idea that samples collected before and after the end of 2000 are different. The statistical significance is strong enough that further data analysis evaluates each period separately.

The possibility that the apparent trend represents a sampling artifact rather than an actual environmental change led to a closer examination of the sampling protocol and whether or not there were any changes between 2000 and 2001 that may have contributed to the observed differences. As it happens, there was such a change.

The duplicate sampling site for PCBs was moved from the former Fox River UATM sampling site to Wisconsin Rapids in June, 1997, where it remained until that site was discontinued in June, 2000. At that time, a second sampler was installed at the current Green Bay PCB sampling site, where it has remained through the end of 2003.

Initially, this second sampler was used only for duplicate samples. However, beginning in October 2000, samples were collected approximately equally between the two samplers. A t-test was performed to compare results obtained with the original sampler and those obtained with the duplicate sampler (Table R-7). This comparison was conducted between the sets of individual sample results, rather than time weighted averages.

Table R-7: Statistical Comparison between Green Bay Samplers

Sampler	Mean	Variance	Observations	df	P(T<=t) two-tail
Original	0.18	0.010	45	81	0.330
New	0.20	0.008	39		

Note that the P value indicates a low likelihood that the data sets and that the mean result obtained using the new sampler is higher. Hence the lower values observed after 2000 are unlikely to be an artifact related to the change in protocol.

One explanation for the drop in concentration is the remediation project begun in 1999 and completed in 2000. Ambient concentrations may have declined in response to the removal of PCB contaminated sediments from the river. If so, the data provide evidence of the benefits of remediation efforts in reducing impacts from historic contamination.

Seasonal Trends

Data from all sites is sufficient for an analysis of seasonal trends. All data collected during the course of the project is included in this analysis. The table below presents time weighted average seasonal mean concentrations obtained from each of the sites. Reporting format is the mean ± the standard deviation in ng/m^3, followed by the number of samples in parenthesis. Values were obtained using the descriptive statistic data analysis tool in Microsoft Excel.

Note that "winter" contains the samples collected between December and February, "spring" between March and May, "summer" between June and August, and "fall" between September and November. Green Bay results are separated into the sampling periods discussed in **Annual Trends**. The Parkway School results for summer are evaluated both with and without the statistical outlier. Madison values are calculated with the non-detects evaluated at the detection limit.

First, note that the general trend of SS>HQ>PS (no out)≈GB>ME noted in Table R-1 continues in all seasons. In addition, each site displays a general trend of Summer > Spring ≈ Fall > Winter to varying degrees. Also, the standard deviation of the data obtained from 16th Street varies far more than the other sites, with the exception of the single outlier observed at the Parkway School site.

Winter concentrations observed at the 16th Street site are about equal to the summer concentrations in Green Bay, while winter SER Headquarters results are about equal to spring values in Green Bay. These facts may confirm that the PCB point source near 16th Street has an observable impact on the local environment, and that the effect is observable several miles away at the SER Headquarters site.

Finally, note the symmetry of the seasonal concentrations observed at Madison East. The values observed at Madison East conform closely to those obtained in Wisconsin Rapids between 1997 and 2000. As there are no known local sources at either site, these values may represent realistic seasonal urban background concentrations for the region.

Table R-8: Seasonal Mean PCB Concentrations (ng/m3 ± sd (N))

Site	Winter	Spring	Summer	Fall
SS	0.26 ± 0.20 (31)	0.45 ± 0.28 (25)	0.65 ± 0.30 (31)	0.40 ± 0.26 (34)
HQ	0.15 ± 0.07 (8)	0.25 ± 0.07 (7)	0.48 ± 0.07 (7)	0.28 ± 0.16 (10)
PS	0.09 ± 0.04 (9)	0.17 ± 0.06 (7)	0.58 ± 0.69 (7)	0.22 ± 0.14 (8)
PS no out			0.33 ± 0.12 (6)	
GB, 97-00	0.12 ± 0.05 (20)	0.28 ± 0.11 (24)	0.34 ± 0.14 (30)	0.28 ± 0.11 (32)
GB, 01-03	0.09 ± 0.02 (24)	0.16 ± 0.11 (20)	0.26 ± 0.07 (24)	0.17 ± 0.06 (23)
ME	0.05 ± 0.01 (10)	0.10 ± 0.01 (6)	0.20 ± 0.06 (13)	0.10 ± 0.06 (14)

T-tests were use to compare seasonal means of individual sites. Reported parameters include the mean, variance and number of samples (on the left hand half of the table), and the degrees of freedom (to the right and above the asterisks on the right side of the table) and t-test P-values (to the left and below the asterisks). P values of 0.05 or less are tabulated in ***italicized boldface***.

The tables indicate that the apparent seasonal differences are strongly statistically significant. In general, Summer > Spring ≈ Fall >Winter. The Parkway School site does not quite conform to this general observation with adequate statistical significance. The reason for this is a combination of the few number of samples, and the widely variable values observed in summer.

It is important to note that the degree of statistical significance noted between the seasons at each site are similar, in spite of the fact that far fewer samples were collected at the Parkway School, SER Headquarters and Madison sites. The variability of the data from the 16th Street site requires a larger sample size for differences to become statistically significant.

Seasonal data from each site is shown in the box and whisker plots on the pages following the tables.

Further investigation of seasonal trends is made through comparing the sites within each season. This analysis is conducted to determine whether the differences between the sites reported in Table R-8 are significant. These comparisons are shown in tables R-15 through R-18 following the figures.

Note that most differences between the sites during the different seasons are statistically significant. Some exceptions to this general rule are important. Data from the Green Bay site are indistinguishable from those obtained at the Parkway School site in all seasons, while the results from the SER Headquarters site are indistinguishable from those of the Green Bay and Parkway School sites in winter and fall.

Table R-9: Statistical Comparison of Seasonal Concentrations at 16th Street

SS	Mean	Variance	Samples	Winter	Spring	Summer
Winter	0.26	0.038	31			
Spring	0.45	0.081	25	***0.008 (41)***		
Summer	0.65	0.092	31	***2.3E-07 (51)***	***0.014 (53)***	
Fall	0.40	0.070	34	***0.018 (60)***	0.534 (50)	***0.001 (60)***

Table R-10: Statistical Comparison of Seasonal Concentrations at SER HQ

HQ	Mean	Variance	Samples	Winter	Spring	Summer
Winter	0.15	0.004	8			
Spring	0.25	0.005	7	***0.012 (13)***		
Summer	0.48	0.005	7	***9.7E-07 (12)***	***5.8E-05 (12)***	
Fall	0.28	0.027	10	***0.033 (12)***	0.558 (13)	***0.006 (13)***

Table R-12: Statistical Comparison of Seasonal Concentrations at Parkway School

PS	Mean	Variance	Samples	Winter	Spring	Summer	SumNo
Winter	0.09	0.002	9				
Spring	0.17	0.003	7	***0.012 (11)***			
Summer	0.58	0.479	7	0.109 (6)	0.164 (6)		
SummerNo	0.33	0.015	6	***0.004 (6)***	***0.024 (7)***		
Fall	0.22	0.020	8	***0.034 (8)***	0.336 (10)	0.224 (6)	0.171 (12)

Table R-13: Statistical Comparison of Seasonal Concentrations in Green Bay

Period	Season	Mean	Variance	Samples	Winter	Spring	Summer
97-00	Winter	0.12	0.002	20			
	Spring	0.28	0.013	24	***1.8E-07 (32)***		
	Summer	0.34	0.018	30	***7.2E-10 (39)***	0.142 (52)	
	Fall	0.28	0.011	32	***1.3E-09 (47)***	0.853 (48)	0.077 (55)
01-03	Winter	0.09	0.000	24			
	Spring	0.16	0.012	20	***0.028 (20)***		
	Summer	0.26	0.006	24	***8.6E-11 (27)***	***0.001 (32)***	
	Fall	0.17	0.004	23	***3.9E-05 (26)***	0.724 (30)	***4.8E-05 (45)***

Table R-14: Statistical Comparison of Seasonal Concentrations in Madison

ME	mean	variance	samples	Winter	Spring	Summer
Winter	0.05	6.8E-05	10			
Spring	0.10	1.6E-04	6	***1.3E-05 (8)***		
Summer	0.20	0.004	13	***5.5E-07 (13)***	***5.1E-05 (14)***	
Fall	0.10	0.003	14	***0.002 (14)***	0.907 (16)	***1.8E-04 (24)***

Figure R-3: Sixteenth Street Seasonal Trends

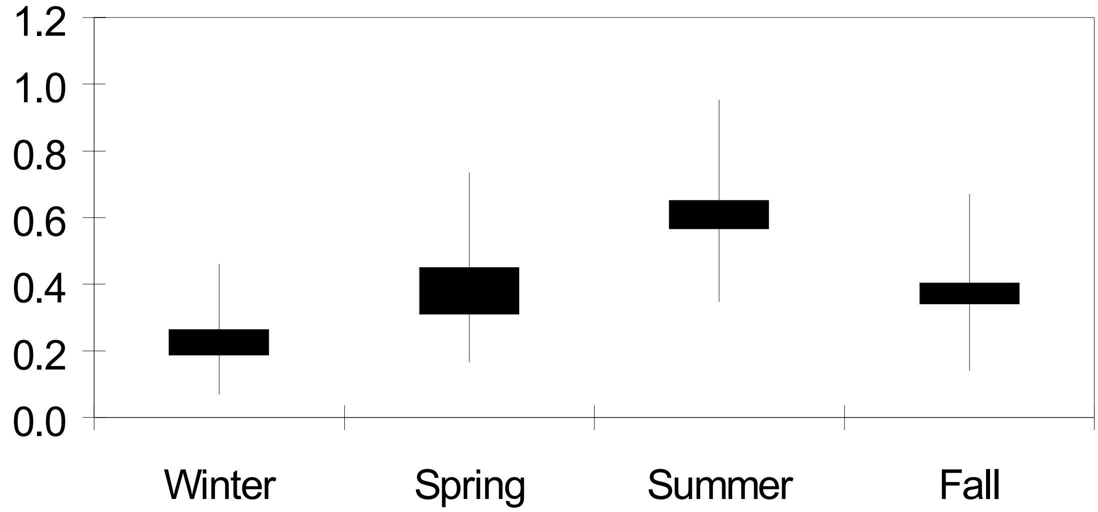


Figure R-4: SER Headquarters Seasonal Trends

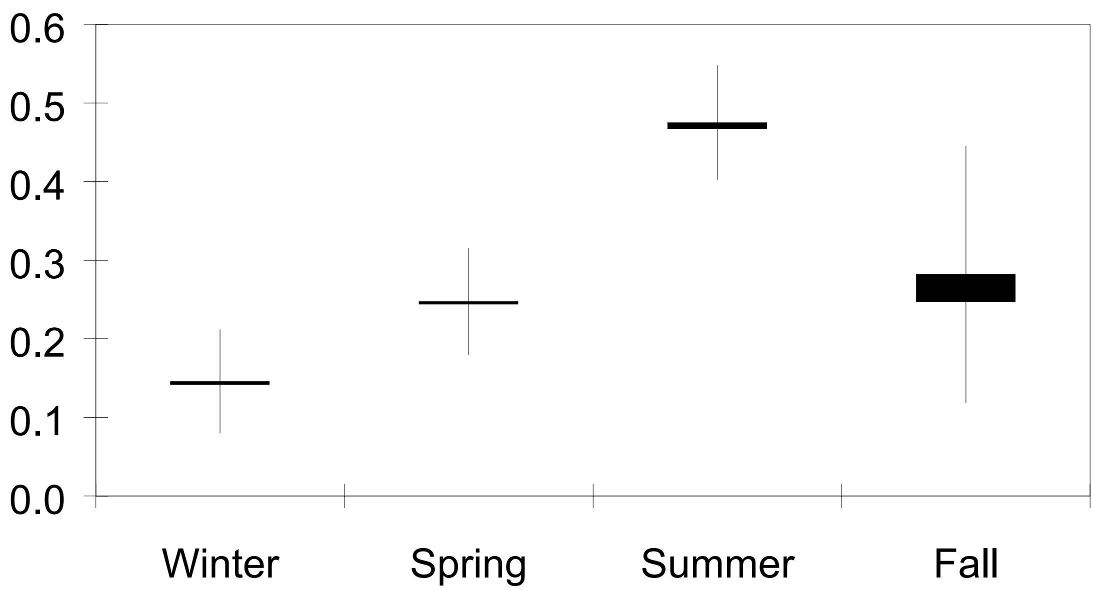


Figure R-5: Parkway School Seasonal Trends

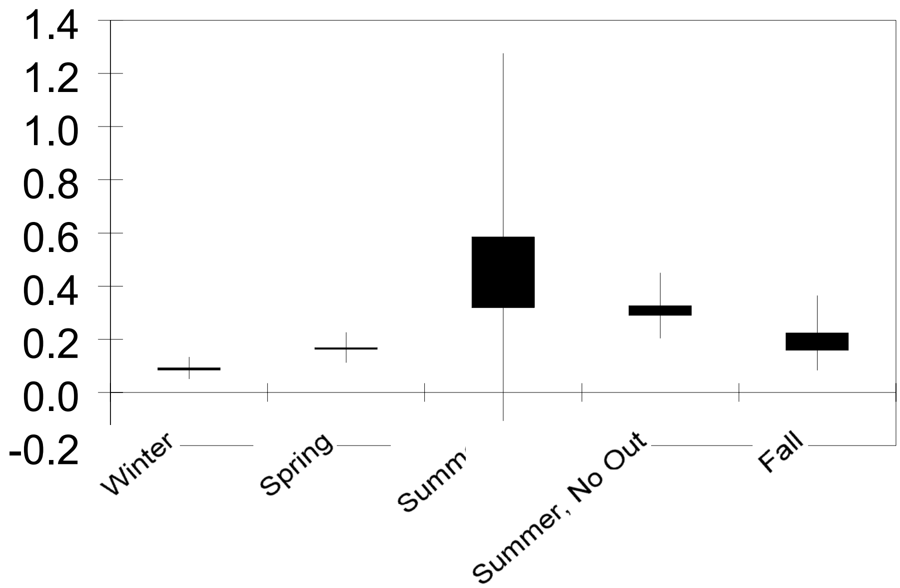
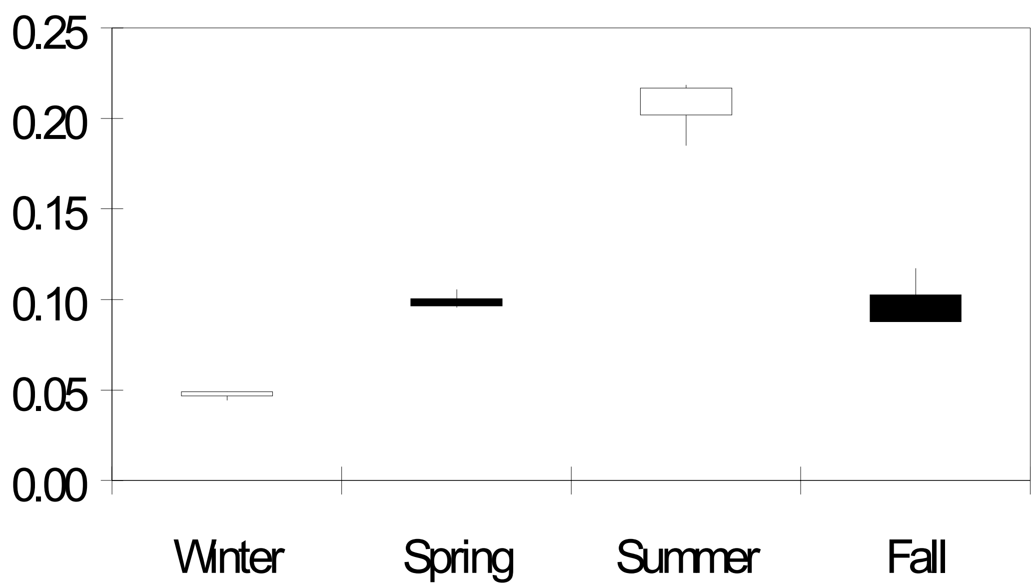


Figure R-6: Madison East Seasonal Trends



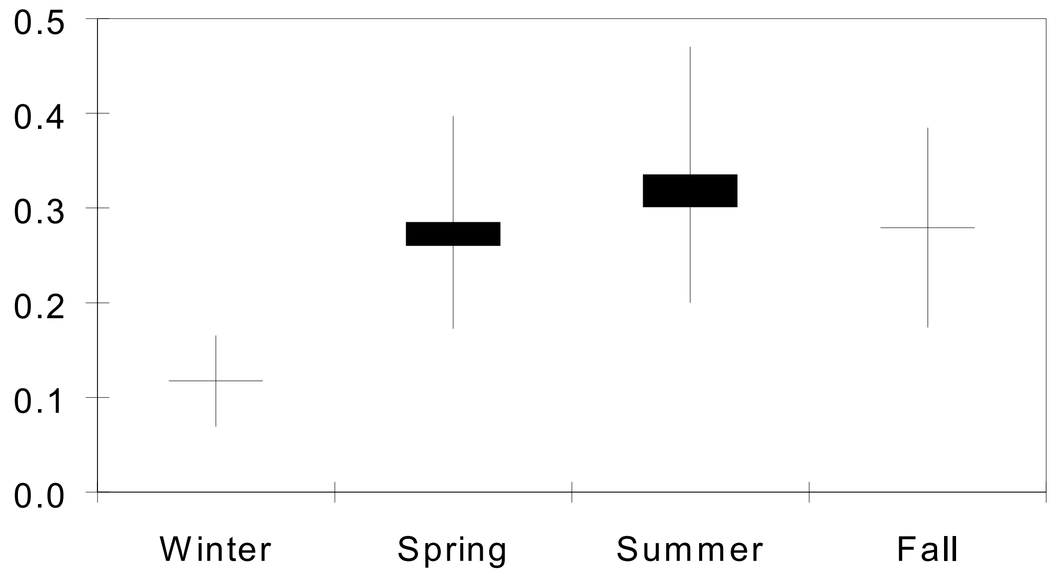


Figure R-7: Green Bay Seasonal Mean PCB Values, 1997 - 2000

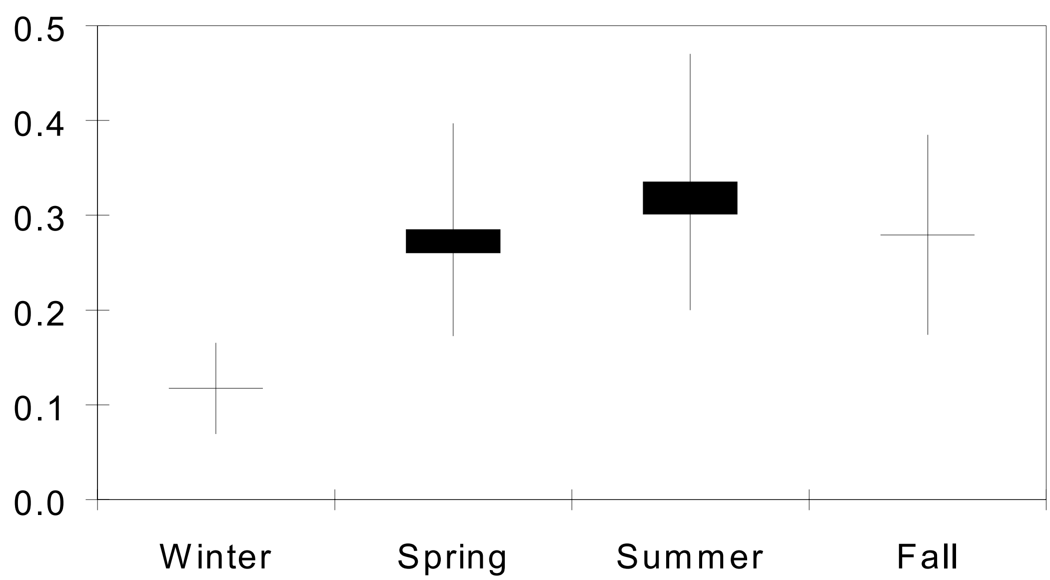


Figure R-8: Green Bay Seasonal Mean PCB Values, 2001 - 2003

Table R-15: Inter-site Statistical Comparison of Winter Concentrations

Site	Mean	Variance	Samples	SS	HQ	PS	GB 01-03
SS	0.26	0.038	31				
HQ	0.15	0.004	8	***0.008 (34)***			
PS	0.09	0.002	9	***5.4E-05 (37)***	0.075 (11)		
GB 01-03	0.09	0.000	24	***3.9E-05 (31)***	0.070 (10)	0.862 (7)	
ME	0.05	0.000	10	***8.4E-07 (30)***	***0.004 (7)***	***0.010 (9)***	***7.0E-11 (32)***

Table R-16: Inter-site Statistical Comparison of Spring Concentrations

Site	Mean	Variance	Samples	SS	HQ	PS	GB 01-03
SS	0.45	0.081	25				
HQ	0.25	0.005	7	***0.003 (30)***			
PS	0.17	0.003	7	***7.5E-05 (29)***	***0.037 (12)***		
GB 01-03	0.16	0.012	20	***3.9E-05 (33)***	***0.019 (18)***	0.678 (21)	
ME	0.10	0.000	6	***2.6E-06 (24)***	***0.001 (6)***	***0.018 (7)***	***0.045 (20)***

Table R-17: Inter-site Statistical Comparison of Summer Concentrations

Site	Mean	Variance	Samples	SS	HQ	PS	PS - out	GB 01-03
SS	0.65	0.092	31					
HQ	0.48	0.005	7	***0.007 (36)***				
PS	0.58	0.479	7	0.811 (7)	0.692 (6)			
PS - out	0.33	0.015	6	***3.2E-04 (19)***	***0.032 (8)***			
GB 01-03	0.26	0.006	24	***4.0E-08 (35)***	***4.0E-05 (10)***	0.257 (6)	0.231 (6)	
ME	0.20	0.004	13	***2.8E-09 (35)***	***3.8E-06 (11)***	0.194 (6)	0.057 (6)	***0.022 (29)***

Table R-18: Inter-site Statistical Comparison of Fall Concentrations

Site	Mean	Variance	Samples	SS	HQ	PS	GB 01-03
SS	0.40	0.070	34				
HQ	0.28	0.027	10	0.089 (24)			
PS	0.22	0.020	8	***0.014 (21)***	0.427 (16)		
GB 01-03	0.17	0.004	23	***1.1E-05 (34)***	0.053 (10)	0.288 (8)	
ME	0.10	0.003	14	***1.9E-07 (39)***	***0.007 (10)***	***0.047 (8)***	***0.004 (31)***

Aroclor Trends

The method employed to identify and quantify PCBs involves selecting a number of characteristic chromatographic peaks and comparing these with laboratory prepared standards of commercial aroclor mixtures. Most samples collected throughout the UATM PCB monitoring program have been identified and quantified as Aroclor 1242, a mixture that was commonly used in electrical components and carbon-less copy paper.

A problem with this method of identification is that PCB congener peaks that may be present in environmental samples but are not part of the standard mixture that most closely resembles the sample are not quantified. These "extraneous" chromatographic peaks are not identified, or included in the analysis.

During the summer of 2002, the PCB analyst at the State Lab of Hygiene noticed that there were a number of samples where the Aroclor 1242 pattern was not as well conformed to as most samples. At that time, he investigated the patterns developed by a variety of other commercial aroclor mixtures, as well as combinations of these mixtures. While no single or combination of aroclors precisely matched the patterns observed in the samples, the best fit was obtained with a mixture of Aroclors 1242, 1248 and 1254. Reporting of results since that time has included whether the sample was identified as Aroclor 1242, or the more complex mixture.

Identification of aroclors obtained for results from 2002 and 2003 are summarized in the following table. Parameters reported include the number of samples identified as each mixture, the percentage this represents of the total number of samples, and the total number of samples included in this analysis.

Table R-19: Summary of Aroclor Identification, 2002 - 2003

Site	Aroclor 1242		Aroclor 1242/1248/1254		Samples
SS	33	80.5%	8	19.5%	41
HQ	17	68.0%	8	32.0%	25
PS	4	16.7%	20	83.3%	24
GB	43	82.7%	9	17.3%	52
ME	19	57.6%	14	42.4%	33

Note that differences between the sites are apparent here as well, with the majority of Sixteenth Street samples identified as Aroclor 1242, and the majority of the Parkway School site samples identified as the mixture of Aroclors 1242, 1248 and 1254. The SER Headquarters identifications are in between these two extremes, while still tending towards Aroclor 1242. This information is important, as it provides evidence that the PCBs observed at Parkway School and Sixteenth Street are probably coming from different sources, while the Headquarters site is affected by both.

Aroclor 1242 is a relatively light and volatile mixture of PCB congeners, while Aroclors 1248 and 1254 are progressively heavier and less volatile. This information makes a seasonal comparison of identifications worthwhile. The following table presents a seasonal summary of PCB identifications by site. Results are tabulated with the number of samples identified as Aroclor 1242 per site per season followed by the number of samples identified as the mixture of Aroclors 1242, 1248 and 1254.

Table R-20: Seasonal Summary of Aroclor Identification, 2002 - 2003

Site	Winter	Spring	Summer	Fall
SS	6 / 0	9 / 0	9 / 6	9 / 2
HQ	4 / 0	6 / 0	2 / 5	5 / 3
PS	3 / 2	1 / 5	0 / 7	0 / 6
GB	8 / 0	13 / 0	10 / 8	12 / 1
ME	5 / 0	5 / 0	3 / 10	6 / 4

Note that with the exception of the Parkway School site, all winter and spring PCBs have been identified as Aroclor 1242. This makes sense when one considers that the 1242 congeners are more readily volatilized. What is interesting is that in spite of this fact, a significant portion of the results from Parkway School includes enough of the heavier, less volatile congeners to be identified as the mixture of Aroclors 1242, 1248 and 1254.

This information clarifies and reinforces the idea that separate sources are impacting the Milwaukee sites.

Summary of Findings

To summarize the pertinent points that have been discussed in this section:

1) Ambient PCB concentrations at different locations in Milwaukee, Green Bay and Madison are significantly different. The overall trend in results indicates the following relationship: **SS > HQ > PS ≈ GB > ME**

2) Data from Green Bay reveals a marked decrease in annual mean concentration following 2000, which may be related to the removal of contaminated sediments from the Fox River performed in 1999 and 2000.

3) Data from the Sixteenth Street site is more variable than that from Green Bay, but fails to show a distinguishable trend in its variation.

4) Significant seasonal trends are present at all sites. The general trend observed follows the relationship: **Summer > Spring ≈ Fall > Winter**.

5) Inter-site comparisons on a seasonal basis follow the same general trend illustrated in point one above, with the exception that winter and values from SER Headquarters are indistinguishable from those obtained at the Parkway School and Green Bay sites.

6) Identification of different PCB mixtures in the samples indicates that the Parkway School and Sixteenth Street sites are influenced by different sources.

Spatial Distribution of Airborne PCBs in Milwaukee, Wisconsin
Source Analysis

In the former section, calculations were based on time weighted average values. In this section, calculations are on a per sample basis. Individual samples are compared in the context of parameters, such as temperature and wind.

Inter-Site Comparison

Site summary statistics (evaluated on a per-sample basis) and distribution data (percent of samples greater than 0.05, greater than 0.3 and greater than 1.0 ng/m^3) are presented in Table S-1.

Table S-1: Site Statistics for Inter-site Comparison

	SS	HQ	PS	PSno	GB	ME
Average	0.48	0.32	0.32	0.24	0.21	0.14
Max	1.49	0.60	2.13	0.56	0.59	0.34
Min	0.05	0.07	0.06	0.06	0.06	0.04
RSD (%)	63.4%	49.9%	128.2%	51.9%	51.0%	54.8%
N =	93	25	24	23	103	34
> 0.05	100.0%	100.0%	100.0%	100.0%	100.0%	85.3%
> 0.30	68.8%	52.0%	29.2%	26.1%	18.4%	2.9%
> 1.0	8.6%	0.0%	4.2%	0.0%	0.0%	0.0%

Per sample averages differ slightly from time weighted averages, but the trends are consistent. Individual sample results at all sites other than 16th Street are subtracted from the 16th Street values for the same sampling period. The averages of the differences are presented in Table S-2. The results demonstrate that levels are consistently higher at 16th Street. In fact, there are more instances when 16th Street concentrations exceed those of other sites by more than 1 ng/m^3 that there are occurrence of values greater than 1 ng/m^3 observed at the other sites.

Table S-2: 16th Street Results Relative to Each Site, by Sample

	SS-HQ	SS-PS	SS-PSno	SS – GB	SS-ME
Average	0.28	0.28	0.36	0.28	0.47
N =	24	23	22	90	29
> 1.0	4.2%	8.7%	9.1%	2.2%	6.9%

The fact that three sites were collecting samples in Milwaukee simultaneously provides the opportunity to evaluate the results relative to both an urban average, composed of all results obtained during a particular sampling event, and relative to the urban minimum. Both of these evaluations are intended to provide a basis by which the local source contribution beyond the urban background can be calculated.

The use of urban average values is a relatively conservative way to measure local impacts, while the use of the sampling period minimum assumes that this value more closely represents the urban background, and maximizes the potential contribution of local sources to the results. Both of these values are used in the correlation and regression calculations to further characterize site differences.

The table below summarizes the per sample urban average and urban minimum concentrations in Milwaukee. All 27 sample periods for which more than one result is available in Milwaukee were included in this analysis.

Table S-3: Per Sample Urban Average and Urban Minimum Summary

	Urban Average	Urban Average, no outlier	Urban Minimum
Average	0.39	0.37	0.24
Max	1.05	0.70	0.56
Min	0.10	0.10	0.06
RSD (%)	54.9%	46.4%	53.9%
> 0.05	100.0%	100.0%	100.0%
> 0.30	59.3%	59.3%	29.6%
> 1.0	3.7%	0.0%	0.0%

Table S-4 summarizes results from each Milwaukee site relative to the urban average, and the urban average excluding the Parkway School outlier. This comparison frequently yields negative values. With the exception of the outlier, no samples collected at SER Headquarters or Parkway School exceed the urban average by more than 0.05 ng/m^3.

Table S-4: Site Results Relative to Urban Average Summary

	Relative Urban Average			Relative Urban Average, no Outlier		
	SS	**HQ**	**PS**	**SS**	**HQ**	**PS**
Average	0.17	-0.09	-0.09	0.19	-0.07	-0.14
Max	0.74	0.05	1.08	0.74	0.05	0.03
Min	-0.49	-0.59	-0.44	-0.03	-0.31	-0.44
RSD(%)	147.9%	-154.1%	-310.5%	113.0%	-137.8%	-95.7%
Samples	26	25	24	26	25	23
> 0.05	16	0	1	16	0	0
> 0.30	5	0	1	5	0	0
> 1.0	0	0	1	0	0	0

Table S-5 summarizes the site results relative to the urban minimum, including number of samples (N =). There are only 3 periods where Parkway School did not have the minimum concentration. One is the outlier (discussed above). It is noteworthy that the other two occurred in November and December 2003. These samples were collected after the draw down of the Estabrook Impoundment to its winter level.

Table S-5: Site Results Relative to Urban Minimum Summary

	SS	HQ	PS	PS – Out
Average	0.33	0.07	0.07	0.00
Max	1.18	0.19	1.67	0.05
Min	0.00	0.00	0.00	0.00
RSD(%)	102.1%	86.1%	459.8%	331.3%
Samples	26	25	24	23
Minimum	3	3	21	21
> 0.05	20	13	3	2
> 0.30	12	0	1	0
> 1.0	2	0	1	0

Correlations and Regressions

Evaluation of the PCB results relative to other potentially significant environmental considerations is achieved through the correlations and linear regressions using Microsoft Excel data analysis tools. The concentration data used include each individual result and the result relative to the sampling period's urban average and minimum. This section discusses these comparisons in Milwaukee, while the following section discusses the comparison sites in Green Bay and Madison. All tables showing the results of these analyses are presented together, along with attempts to interpret the relationships observed in light of the known sources.

The correlation coefficient is a measure of the tendency of two data sets to vary in relation to each other and does not imply cause. The level of significance assigned to correlation coefficients is based on the size of the data set.

Regression analysis evaluates the strength of the linear relationship between data sets. The regression factor (R^2) reported below indicates the proportion of the variability which can be attributed to each factor. Analysis results indicate that only the relationship between concentration and temperature can describe more than 50% of the variability in concentration levels.

Non-PCB data used in these calculations include wind speed and wind direction (vector mean average) and on an hourly wind sector basis. Temperature is incorporated using the established relationship between the natural log of the PCB concentration and the inverse of the temperature in degrees Kelvin (LN PCB vs. 1/T).

Additional factors evaluated include the daily average water flow rates for the Milwaukee River at the Estabrook dam and Lincoln Creek. Emission inventory data for Miller Compressing are included in the examination of Sixteenth Street data (between 2000 and 2002).

Factors included in the Green Bay and Madison comparisons include wind speed and wind direction on a sample period vector mean averaged basis, air temperature, and, in the case of Green Bay data, Fox River flows and temperatures. The Green Bay data is separated into the distinguishable sampling periods, with results from samples collected between 1997 and 2000 evaluated separately from those collected between 2001 and 2003.

Regression factors obtained during this analysis are summarized in Table S-6.

Table S-6: Significant Regression Factors

Parameter	SS Amb	HQ Amb	PS Amb	PS Amb - Out	GB 97 - 00	GB 01 - 03	ME
LN vs 1/T	0.318	0.784	0.662	0.776	0.474	0.653	0.833
N =	92	25	24	23	93	78	34

Most sites show a fairly strong linear relationship comparison, with regression factors ranging from 0.318 to 0.833. This is not unexpected. Numerous studies regarding the atmospheric concentrations of PCBs and similar compounds demonstrate this relationship. This is generally interpreted to mean that temperature drives volatilization of these materials. This relationship is a cornerstone of the environmental cycling model. With this in mind, it becomes important to note the exceptions to the general relationship with temperature.

The most significant exception to this relationship is seen in the data from the Sixteenth Street site. There is no linear relationship between temperature and ambient concentration of PCBs at this site (R^2 = 0.318). This is likely to be a result of the local point source, which emits PCBs when waste containing them is shredded, a factor not related to temperature.

The second exception is presented by the Green Bay data collected between 1997 and 2000. In this case, there is not enough information about potential local point sources to explain the lack of a relationship. Data from samples collected after 2000 do show significant linearity (R^2 = 0.653).

Significant correlations between meteorological parameters and PCB concentrations are presented in Table S-7. These are all co-variance relationships above the 95% confidence level.

Table S-7: Significant Correlation Coefficients

Parameters	N	WS	WD	1/T
SS	92	-0.234	-0.391	-0.564
SS Rel Avg			-0.486	
SS Rel Min			-0.536	
HQ	25	-0.420		-0.886
HQ rel Min		-0.448		-0.437
PS All	24			-0.813
PS - Out	23			-0.881
PS - Out Rel Avg			0.560	
GB 97 - 00	93		-0.272	-0.689
GB 01 - 03	78		-0.308	-0.808
ME	34			-0.905

Wind has a negative correlation with PCB concentrations at the Sixteenth Street and SER Headquarters sites. This indicates that as wind increases, concentrations decrease. This is true for a number of pollutants, as calm conditions can allow pollutants to accumulate. This relationship is further explored in the sector analysis following.

Wind direction is consistently correlated with PCB concentration at the Sixteenth Street and Green Bay sites. In both cases, the correlation is negative, indicating that as the wind direction (in degrees) increases, concentration decreases. In addition, there is a positive correlation with wind direction at Parkway School, when the outlying value is excluded, and results are considered relative to the urban average.

These results are difficult to interpret. One problem is related to vector mean averaging of wind speed and direction over the course of the three or six day sample periods. During a period of several days the wind is likely to come from a number of different directions, confusing source contributions from a given direction.

For this reason, the Milwaukee data are subjected to a more thorough analysis. The percentage of time the wind was coming from each compass sector is compared with site concentrations. Hourly wind data for Green Bay were not available, so this further analysis is not possible at this time.

Table S-8 below provides all of the significant correlation coefficients derived from the met sector analysis of the Milwaukee data.

Table S-8: Milwaukee Met Sector Correlation Analysis

Parameters	Calm	N	NE	SE	S	SW	W	NW
SS	0.246	0.469	0.306		-0.227	-0.224	-0.382	
SS Rel Avg		0.479	0.481		-0.385			
SS Rel Min		0.507	0.503					
HQ	0.549			0.500				-0.549
HQ Rel Min							-0.448	-0.425
PS - Out	0.677			0.560			-0.460	-0.496
PS-out rel avg		-0.466	-0.45					

The Sixteenth Street data show a number of significant correlations. First, the negative correlation with wind speed (Table S-7) is confirmed by a positive correlation with calm conditions. As noted above, this phenomena is relatively common with air pollutants.

Positive correlations are observed between ambient concentrations, both direct and relative to the urban averages and minimums, and winds from the north and north east. This correlation may reflect that the monitoring site is located south of Miller Compressing and the Menominee valley. The negative correlation between PCB concentration winds from the south, southwest and west may reflect a lack of significant sources in those directions.

Data from the SER Headquarters show fewer significant correlations. Calm conditions and winds from the south east are positively correlated with PCB concentrations, while negative correlation is observed with winds from the west and northwest. These observations are interesting, in that the known sources being investigated are located to the southwest (Miller Compressing) and the northwest (Estabrook Impoundment).

The negative correlation between PCB concentration and wind from the direction of the Estabrook Impoundment is probably due to the distance between SER Headquarters and the impoundment. The lack of a correlation with winds from the southwest, however, weakens the argument that point source impacts are observable at this site.

The positive correlation with winds from the southeast (in the direction of the city center) could indicate that another unknown source is impacting this site, or could reflect the fact that the shortest distance to the Milwaukee River from this location is to the southeast. There has been no attempt to locate information concerning the PCB content of the Milwaukee River and its sediments downstream of Estabrook dam.

Data from Parkway School is positively correlated with calm conditions and winds from the southeast. Calm conditions and their effect on pollutants has been discussed. The correlation with southeast winds, and lack of correlation with more southerly winds is somewhat surprising, as the suspected primary source (Lincoln Park lagoon) is located directly to the south of the school.

Parkway School is located fairly close to the Milwaukee River to the southeast, but is even closer to the northeast, while the low water dam (that may increase volatilization of PCBs through aerating the water column) is located directly north. That the observed concentrations relative to the urban averages show a negative correlation with winds from the north and northeast confounds this analysis further. In addition, the data from Parkway School shows a negative correlation with winds from the west and northwest. As there are no known close sources in those directions, this particular result is not surprising.

Summary of Findings

Pertinent conclusions which can be drawn from the data presented in this section are summarized below.

1) Ambient concentrations at the Sixteenth Street site are consistently higher than those at other sites in Milwaukee and around the state. Per sample differences between Sixteenth Street and the other sites average 0.28 ng/m^3 or greater. Therefore, the Sixteenth Street site does not provide a realistic urban average PCB concentration for Milwaukee.

2) Regression analysis indicates a significant relationship between PCB concentration and temperature. While most sites show a significant linear relationship with temperature, data from the Sixteenth Street site does not. This may be a result of impacts from the local point source.

3) Correlation analyses results are ambiguous. Few of these analyses demonstrate a strong influence from known sources. It is not clear if this reflects a lack of influence from these sources, or if the data sets are too small.